

“On the Compressibilities of Oxygen, Hydrogen, Nitrogen, and Carbonic Oxide between One Atmosphere and Half an Atmosphere of Pressure, and on the Atomic Weights of the Elements concerned.—Preliminary Notice.” By LORD RAYLEIGH, O.M., F.R.S. Received February 3,—Read February 11, 1904.

The observations now referred to were conducted with an apparatus designed upon the same lines as that already described.* It must suffice to mention that the only important modification lay in the fact that the two single volumes, which, when employed together, constitute the double volume, were used separately and alternately, so as to eliminate in each set of measurements any question as to what the ratio of these volumes exactly is. It is hoped to give a full description of the method when it has been extended to the examination of other gases, such as nitrous oxide and carbonic anhydride. The temperatures ranged from 10°—15°, and care was taken that in each measurement the mean temperatures should be almost exactly the same for the single and for the double volume.

The results were reduced much as previously explained, and give for the values of B , which, according to Boyle's law, should be unity,

Oxygen	1·00040
Hydrogen	0·99976
Nitrogen	1·00017
Carbonic oxide	1·00028

B here denotes the quotient of the value of pv at the half atmosphere by the corresponding value at the whole atmosphere. That it would be less than unity in the case of hydrogen, and exceed unity for the other gases, is what would be anticipated from their behaviour at higher pressures.

If we measure p in atmospheres, and assume, as has usually been done, *e.g.*, by Regnault and Van der Waals, that at small pressures the equation of an isothermal is

$$pv = PV(1 + ap),$$

where PV is the value of the product in a state of infinite rarefaction, then

$$a = 2(1 - B).$$

Probably the chief interest of a knowledge of the coefficient a is

* “On the Law of the Pressure of Gases between 75 and 150 Millimetres of Mercury,” ‘Phil. Trans.’ A, vol. 198, pp. 417—430, 1902.

the application to deduce a correction to the relative densities of gases as observed at atmospheric pressure, so as to determine what would be the relative densities in a state of great rarefaction, to which alone Avogadro's law is applicable.*

Taking oxygen as a standard, we see that the small correcting factor to be introduced in order to pass from the ratio of densities at one atmosphere to that at great rarefaction, is $(1+a)/(1+a_0)$, or $1+2(B_0-B)$, the suffix 0 relating to oxygen, that is, as follows:—

Hydrogen	1·00128
Nitrogen	1·00046
Carbonic oxide.....	1·00024

The double of the first number, viz., 2·0026, represents, according to Avogadro's law, the volume of hydrogen which combines with one volume of oxygen at atmospheric pressure to form water. Direct determinations by Scott gave 2·00245, and Morley, in his later work, found 2·0027, so that there is here a good agreement.

The following table gives the densities of the various gases, referred to oxygen = 16, at atmospheric pressure and at very small pressure, as deduced from my own observations.†

Gas.	Atmospheric pressure.	Very small pressure.
Hydrogen	1·0075	1·0088
Nitrogen	14·003	14·009
Carbonic oxide.....	14·000	14·003

From the researches of M. Leduc and Professor Morley, it is probable that the above numbers for hydrogen are a little, perhaps one thousandth part, too high.

The uncorrected number (14·003) for nitrogen has already been given,‡ and contrasted with the 14·05 obtained by Stas. This question deserves the attention of chemists. If Avogadro's law be strictly true, it seems impossible that the atomic weight of nitrogen can be 14·05.

From the molecular weight of CO, viz., 28·006, we deduce, as the atomic weight of carbon, 12·006.

It should be mentioned that D. Berthelot§ has, meanwhile, calculated very similar numbers, based upon the observations of Leduc.

* The application to oxygen and hydrogen was made in my paper, "On the Relative Densities of Oxygen and Hydrogen," *Roy. Soc. Proc.*, vol. 50, p. 448, 1892; *Scientific Papers*, vol. 3, p. 525.

† *Roy. Soc. Proc.*, vol. 53, p. 134, 1893; vol. 62, p. 204, 1897; *Scientific Papers*, vol. 4, pp. 39, 352.

‡ Rayleigh and Ramsay, *Phil. Trans.*, A, vol. 186, p. 187, 1895.

§ *Comptes Rendus*, 1898.